Electroceramics and the Properties of Ionic Crystals

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The classification of electroceramics, based particularly
on the electric properties of the crystalline phase, is given. It
is shown that the electric properties of electroceramics should be
viewed in connection with the properties of polycrystalline dielec-
trics and of polycrystals of electr on semi-conductors. The charac-
teristics of high-quality ceramic materials and manufactured artic-
les, obtained as a result of new crystal formations, are given.

Ceramic technology has taken an exceptional meaning for the
manufacture, from the same materials, of dielectrics, semi-conduc-
tors, and metals. Powder metallurgy, on one side, and electroceram-
ics, on the other, have become new important branches of industry,
founded on baking processes. In particular, electroceramics have
received wide application in present-day radiotechnical and mea-
suring apparatus, and also in vacuum installations. Ceramic mater-
ials, newly developed in the past few years, are far removed in com-
position from porcelain, which contains clay matter, quartz, and
feldspar. Electroceramics is primarily concerned with pure poly-
crystallic formation, appearing either as oxides of metals -- Al_2O_3,
TiO_2, ZrO_2, La_2O_3, BeO -- or with combination of oxides such as
Mullite $(3Al_2O_3 \cdot 2SiO_2)$, Fosterite $(2MgO \cdot SiO_2)$, or Perovskite
$(CaO \cdot TiO_2)$. The basic properties of these new ceramic materials
depend on the properties of the principal crystalline phase, with

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addition of other materials being necessitated either by the demands of the particular technology used, or employed to neutralize harmful ingredients, such as alkaline oxides.

As to the electrical properties, it is customary to divide electroceramics into a group of materials with linear dependence of polarization on applied voltage (the group containing most known ceramic materials), and into a group with non-linear dependence of polarization on voltage, such as barium titanite [1]. Below are shown the properties of only the first group of materials, which are of practical importance in the manufacture of insulators and high-frequency capacitors.

The dependence of the electrical properties of the ceramic on the structure and on the chemical composition is based primarily on the value of the dielectric constant ε and on tangent δ of the material. Specific volume resistivity characterizes quite accurately the quality of the ceramic, even at high temperatures, and electric stability depends in the first place on macroscopic defects -- the degree of uniformity of the ceramic, and on the absence from it of hidden pores.

A ceramic insulator contains, together with the crystalline phase, an amorphous binder amounting to from 5-10 percent or 50-60 percent, depending on the type of ceramic. The dielectric losses of this binder are most often tied in with the structural polarization of the random-disposed weakly-bound ions. Thus the dielectric losses of a ceramic rod at various relationships of the crystalline and amorphous phases are of different types. However, even in purely crystalline state it is necessary to distinguish not one, but several types of dielectric losses, differing among themselves in principle:

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1. Structural losses, due to uneven orientation of ions in the crystal lattice, when there are energy levels of the ion which prevent it from being in a fixed state. These losses are to a known extent similar to those structural losses peculiar to the amorphous state [2]. *Reference*

2. Losses due to the nature of the ionic crystal as an electron semi-conductor [3]. *Reference*

3. Losses due to distributed electric conductivity [4]. *Reference*

As is well known, losses due to distributed conductivity can be derived simply from the relationship

$$Tangent\ \delta = \frac{1.8 \cdot 10^{12} \gamma}{\varepsilon f}$$

where γ is the electric conductivity, under constant voltage.

Structural losses can be separated from losses due to electric semi-conductors by measuring the electric characteristics of the samples after firing them in various gaseous media, for example in an atmosphere of oxygen and and atmosphere of hydrogen or carbon monoxide, and also by investigating the effects of the mixtures, which appear as metallic oxides.

Investigations of the crystalline properties of the ceramic rod require the exclusion of the effects of the amorphous phase. It is generally recognized that the ions of the alkaline metals in the composition of inorganic glass have an unfavorable effect on the magnitude of the dielectric losses.

Comparison of the composition of "radioporcelain" and "ultra-porcelain" shows that in the first there are basic oxides up to 0.6

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percent, and in the secondup to 1.5 percent. Among the two, the dielectric losses of radioporcelain are known to be not less, but more than of ultraporcelain.

The mineral content of these materials is different: Radioporcelain is characterized by the presence of mullite with a basically crystalline phase, while ultraporcelain contains α -earthally clay (corrundum). It is curious that radioporcelain prepared not from mineral raw material, but from pure oxides containing less than 0.2 percent alkalis, shows a tangent δ not less than commercial grade radioporcelain. Figure 1 shows the tangent δ of the investigated materials as a function of temperature. On the same drawing are represented the dielectric losses of baked samples of clays (containing 2.5-3 percent base oxides) and samples of Kaolin (containing less than 0.2 percent base oxides).

All these data show conclusively that the dielectric losses of ceramics, unlike those of glasses, cannot be classified in accordance with the contents of base oxides, if the content of these oxides is less than 1.5-2 percent.

It is possible to deduce that in this case tangent δ is more affected by the crystalline phase than by the glass-like phase.

This situation was confirmed to us by a study of the electric properties of pure crystalline formations, particularly those of mullite, which was shown above to be the basis of radioporcelain, and also of clay and Kaolin in the baked state. The temperature dependence of the dielectric losses of pure mullite is shown in Figure 2.

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The high initial value of tgδ and its sharp increase with temperature explain the unfavorable characteristics of baked Kaolin, as well as the increased value of tg δ of radioporcelain. Changing the gaseous media in heat-treatment of the mullite, and changes in the mixture, have no effect on the dielectric characteristics. It is also well to note the excellent reproducibility of the results in measuring tangent δ and of the volume resistivity of various samples of the ceramics with mullite base, made of various raw materials and heat-treated in various states. Thus mullite is definitely related to crystals as far as structural losses are concerned.

Another crystal with sharply defined structural losses appears to be cordierite, $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$.

The temperature dependence of the dielectric losses of cordierite, synthesized from pure oxides, is also shown in Figure 2.

An entirely different group of crystals is represented by the polycrystals of rutile or corundum (Figure 5). Even in earlier works (1937) we showed that ceramics based on corundum (aluminum oxide) with a high content of crystalline phase did not give consistent values of the angle of the dielectric losses. The reasons for this were not sufficiently clear. The angle of the dielectric losses varied for different samples from below 1 minute to a matter of degrees. Figures 3 and 4 show the temperature dependence of polycrystalline α -clay and rutile in relationship to the gaseous medium in which it was fired. The samples were discs of 20-40 millimeters in diameter and 1-2 millimeters thick, and obtained by baking powdered Al_2O_3 and TiO_2 of technical purity with impurities up to 1.5 percent at temperatures corresponding to 1650-1750 degrees and 1450-1500 degrees Centigrade.

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From the graphs of Figures 3 and 4 follows that the firing of a given group of ceramics should be considered as a complex physico-chemical process, in which not only the temperature, but also the reactions with the surrounding gaseous media have primary significance.

The electric qualities of clay-earth ceramics are lowered only under the action of oxidizing gaseous medium in the process of firing, and, in contrast with titanium-containing ceramics, appear particularly high if firing is done in a highly reducing gaseous medium. It is necessary to add that in the experience of Hartman [3] who defined Al_2O_3 as a semi-conductor of reduction, the result was indicated with some secondary phenomena. As to the negative effects that a reducing gaseous medium has on the electric properties of TiO_2, here undoubtedly occurs a transition of titanium into another valence with resulting different oxide forms, such as Ti_3O_5 and other forms.

It is possible to propose that the anomalies of the dielectric losses of commercial dielectrics manufactured from corundum and rutiles can be explained by their electronic semi-conducting nature. A property of these dielectrics appears to be high volume resistivity, considerably higher than that of ordinary semiconductors. A factor affecting the volume resistivity favorably appears to be the presence in the dielectric sample of even an insignificant quantity of glass separating the individual crystals. Anomalous electric properties of ceramic materials, as related to the group of electronic semi-conductors, become weaker the more amorphous binder it contains, and the more actively this amorphous binder absorbs in its body the unfavorable admixtures. This empirical law finds, naturally, a commercial application.

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In the case of firing of samples of corundum ceramics in a
reducing medium, the amorphous phase is formed more easily, in ac-
cordance with the fact that, for example, ferrous oxide, as known,
appears to be a fusing agent. On the other hand, if the tested
oxides are fired in powder form, rather in the shape of the final
manufacture, particularly low electric qualities result if the gas-
eous medium used for firing is unfavorable, so that the content of
the amorphous phase in the case of powder is very low. Table 1,
listing the electric properties of clay earth fired in an oxidiz-
ing medium, illustrates this point.

TABLE 1

Temperature Degrees Centigrade	Specific Volume Resistivity Ohm-cm.	Tangent of the angle of dielectric losses at $f = 1 \cdot 10^6$ cycles
100	3.10^{10}	0.0270
200	2.10^9	0.0180
300	2.10^8	0.0400

A separate group of mineral formations is represented by
MgO (periclase) $MgO \cdot Al_2O_3$ (spinel) $2MgO \cdot SiO_3$ (Fosterite) and
$MgO \cdot SiO_2$ (Clinoenstatite). The experiment shows that these are
characterized by very high electric qualities regardless of methods
of firing and raw materials used. It appears that materials of
this type are in the class of crystalline dielectrics, to which
also belong the alkaline-halloid crystals. Even the necessary
presence of the amorphous binder in the commercial-grade samples
of a given group causes a difference between the experimentally
observed dielectric losses, and the losses calculated from the
electric conductivity.

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Summarizing, the above data can be classified in accordance with known mineral formation usable in ceramic technology, as in Table 2.

[See Table 2 on following page]

The views developed here can guide practical work in searching for ceramic materials, distinguished by the most diverse characteristics; for example, very high mechanical strength, or high resistance to heat, or very high electric ind*ices*.

To attain high mechanical strength it is necessary to have in the ceramic material a large quantity of the crystalline phase, and some quantity of glass-like phase. Confirming this, a recently developed ceramic material characterized by a resistance to bending up to 6000 kilograms per square centimeter (for cylindrical samples), tangent δ up to 0.0004, and ~~specific~~ dielectric *constant* ~~capacity~~ between 8 and 8.5. The mechanical strength of this new ceramic material exceeds by 5 to 7 times the strength of insulating porcelain and has a strength of the order of structural steels.

A necessary condition for wide technical application of electroceramics, as shown by the experiment, appears to be the simplicity of technology -- firing temperature not higher than 1380-1400 degrees Centigrade, definite plasticity of mass, and sufficiently wide temperature-range of firing. These requirements are fully met by the above mentioned ceramic material, as opposed to the earlier-known ceramic material with enormous mechanical strength -- aluminum oxide.

At the present time it appears possible to solve the problem of furnishing the automotive and aviation industries with high-quality insulators for spark plugs, applying for this purpose the newly-

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TABLE 2

Number of Group	Name of Crystalline Phase of Ceramic		Name of Mineral (Polycrystal)	Chemical Composition	Crystalline System at 20 degrees Centigrade	Electric Properties of Technical Types of Ceramic at t = 20 degrees Centigrade	
						Tangent δ at Radio Frequencies	Specific Volume Resistivity in ohm.cm
I	Polycrystalline Dielectric	(a) No structural Polarization	Periclase	MgO	cubical	< 0.0003	$>10^{18}$
			Spinel	$MgO.Al_2O_3$	cubical	< 0.0003	$>10^{18}$
			Fosterite	$2MgO.SiO_2$	rhombic	< 0.0003	$>10^{18}$
			Clino-enstatite	$MgO.SiO_4$	monoclinical	< 0.0003	$>10^{18}$
		(b) Strong structural Polarization	Mullite	$3Al_2O_3.2SiO_2$	rhombic	0.0020	$10^{13} - 10^{14}$
			Cordierite	$2MgO.2Al_2O_3$ $.5SiO_2$		0.0040	$10^{15} - 10^{16}$
II	Polycrystals - electronic Semi-conductors		Corundum	Al_2O_3	hexagonal	Depending on gaseous medium and admixtures,	$10^{10} - 10^{18}$
			Rutile	TiO_2	tetragonal	$0.0002 - 0.0200$	$10^7 - 10^{15}$
III	Polycrystals - seignette - electric		Perovskite-type	$BaTiO_3$ (Curie point at T=390 degrees K)	tetragonal	0.0160	$10^{13} - 10^{14}$

developed ceramics. Figure 5 shows insulators for automobile
plugs, made of this ceramic. The mechanical strength of such in-
sulators, tested on a typical pendulum-impact machine, corresponds
to an angle of inclination of the pendulum of 140-180 degrees.

Other shapes of the ceramics are very effectively used for
preparation of high-voltage, high-frequency insulators, where it
is necessary to have considerable mechanical strength, low dielec-
tric losses, and ability to withstand high heat (in connection with
hot solder). Figure 6 shows a series of insulators for an effective
working voltage up to 30 kilovolts at frequencies up to 10 megacycles.

Extremely high indexes of ceramics were detected when the
basic materials used were spinel, periclase, fosterite, and Perov-
skite. Of the most importance in obtaining commercial-grade mat-
erials is the proper choice of mineralizers -- insignificant addi-
tions of external matter, which does not form chemical compounds
with either the component materials or with the end products of the
reaction, yet lower the temperature of the reaction.

Figure 7 shows a barrel-type capacitor of ceramic material
with Petrovskite as a base, having a reactive capacity of 50 kilo-
volt-amperes at effective voltage of 10-12 kilovolts, compared with
a similar mica capacitor of the same reactive capacity and the same
high-frequency voltage. The advantages of these capacitors can be
appreciated when they are contrasted with earlier models of the same
overall dimensions,
whose capacity seldom exceeded 5-6 reactive kilovolt-amperes.

Distinguished by an exceedingly high specific reactive capac-
ity, high specific capacity, and simple technology, the capacitors
have a limiting capacity in the finished product not exceeding 100
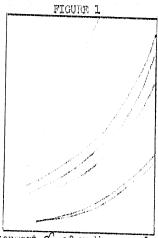
μμfd

~~pico-farad~~. This calls in many cases for the necessity of connecting many individual elements in parallel. Capacitors of high unit capacity are made either in hemispherical or in cylindrical shape. But in normal manufacture of such articles by molding, broaching in the material results in hidden pores and consequently in low electric strength, particularly at high frequencies. Thus, for example, tested voltage gradients of ordinary capacitor material, at ordinary methods, are about 4-5 kilovolt/millimeters at radio frequencies. On the other hand, capacitors with hidden pores are limited as to safe reactive capacity to long waves only, due to the ionization of gas in the pores, resulting in an increasing tangent δ of the capacitor starting at some field *intensity* ~~voltage~~. Figure 8 shows the dependence of tangent δ on the field *intensity* ~~voltage~~ of ceramic capacitors, prepared by two different methods. As shown in Figure 8, in the case of dense material, tangent δ is independent of the field *intensity* ~~voltage~~ up to 8-10 kilovolts per centimeter and correspondingly its reactive capacity exceeds by a factor of 3-4 the reactive capacity of capacitors with hidden pores. Figure 9 shows cylindrical and hemispherical capacitors, prepared in accordance with the new technology which insures high density of the material.

Recently ceramic insulators are gaining an ever wider industrial acceptance replacing paper capacitors not only for high-frequency circuits, but also for low-frequency circuits at constant voltage and for impulse voltages. The values of dielectric *constant* ~~permeability~~ of present-day ceramic capacitors lie between 150 and 7500, which permits the manufacture of miniature capacitors. Figure 10 shows a tubular ceramic capacitor of 80,000 *μμfd* ~~pico-farads~~, designed for a working voltage of 250 volts and intended to replace spark-suppressing paper capacitors.

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In this way ceramic materials based on new crystal formations satisfy the most diverse demands of electric technology.
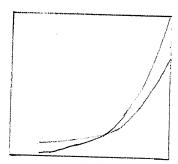
REFERENCES

1. B.M. Vul, "Materials with High and Extra High Dielectric Permeability". Elektrichestvo (Electricity), No. 3, 1946.

2. G.I. Skanavi and A.I. Demeshina, "New Aspect of Dielectric Polarization and Losses in Polycrystalline Dielectrics," ZhETF, No. 1, 1949.

3. F.F. Vol'kenshteyn, Electric Conductivity of Semi-Conductors Gostekhizdat (State Technical Press), 1947.

4. N.P. Bogoroditskiy and V.N. Malyshev, "Dielectric Losses in Crystals" ZhTE, Vol IV, 1036, 1936.

5. N.P. Bogoroditskiy and L.I. Katz, "Aluminum Oxide - Insulating Material for High-Frequency Technology," IEST, No. 3, 1937.

FIGURE 1

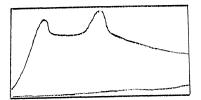Curves showing the tangent δ of radio-porcelain, ultra-porcelain, Kaolin, and clay as a function of temperature, at f = 1 megacycle. 1 - clay; 2 - Kaolin; 3 - radio-porcelain of pure oxides; 4 - radio-porcelain of commercial raw material; 5 - ultra-porcelain of pure oxides; 6 - ultra-porcelain of commercial raw material.

FIGURE 2

Curves showing the tangent δ of mullite and cordierite as a function of temperature at f = 1 megacycle. 1 - mullite; 2 - cordierite.

FIGURE 3

Curves showing the tangent δ of samples of aluminum oxide fired
in various gaseous media as a function of temperature, at f = 1
megacycle. 1 - fired in oxidizing medium; 2 - fired in reducing
medium.

FIGURE 4

Curves showing the tangent δ of polycrystalline rutile, fired in
various gaseous media, as a function of temperature, at f = 1 mega-
cycle. 1 - fired in oxidizing medium; 2 - fired in reducing medium.
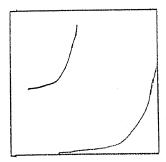
FIGURE 5.

Insulators for sparkplugs of internal-combustion

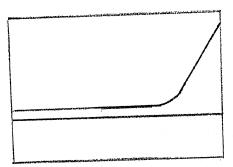engines, made from a new type of mechanically

strong ceramic [Photo]

FIGURE 6.

Samples of high-voltage high-frequency insulators

made of high strength, high-temperature-resisting

electroceramics. [photo]

FIGURE 7.

New type (right) of high voltage barrel-insulator,

equivalent in reactive capacity to a mica capacitor.

[Photo]

FIGURE 8

The tangent δ of ceramic capacitors, prepared by various methods,

as a function of the field intensity, at f = 1 megacycle (accord-

ing to data from LETI). 1 - observed concealed pores; 2 - dense

structure.

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FIGURE 9.

New types of high-voltage ceramic capacitors with increased electrical strength -- hemispherical and cylindrical of capacitance of 1000 pico-farads, and barrel-type (center) pressed in plastic, with capacitance of 500 pico-farads, at test voltage of 15 kilovolts. [Photo]

FIGURE 10.

Tubular ceramic capacitor of capacity 80,000 pico-farads (below) to replace a paper arc-suppressing capacitor. [Photo]